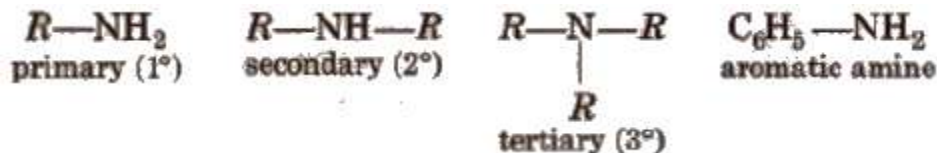


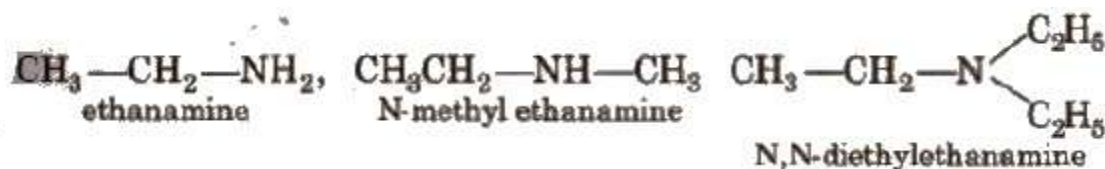
# Chemistry Notes for class 12 Chapter 13

## Amines

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of  $\text{NH}_3$  molecule by alkyl/aryl group(s).

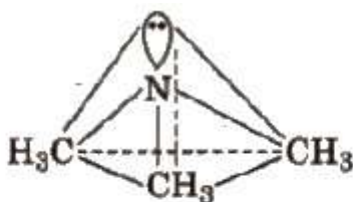


In the IUPAC system, the amines are regarded as alkanamines, e.g.,

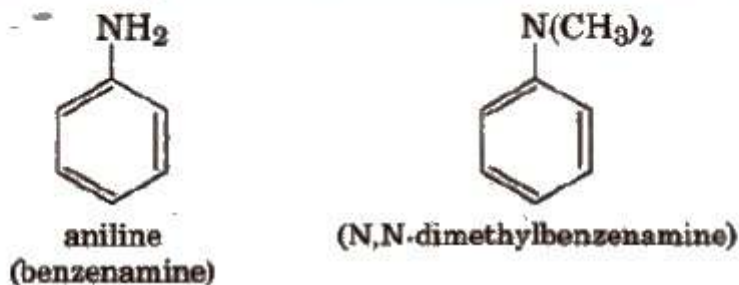


### Structure

The nitrogen atom in amine is  $sp^3$ -hybridised. The three hybrid orbitals are involved in bond formation and one hybrid atomic orbital contains the lone pair of electrons, giving the pyramidal geometry of amines.



In arylamines,  $-\text{NH}_2$  group is directly attached to the benzene ring.

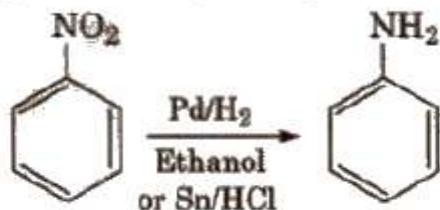


### Methods of Preparation of Amines

### (i) Reduction of nitro compounds

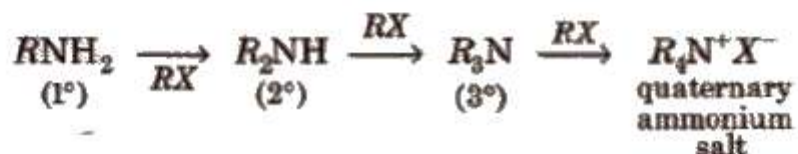
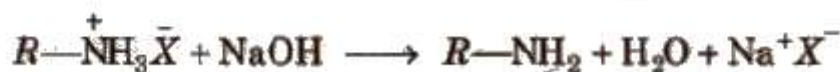


Reduction can take place by Sn/HCl, Ni/H<sub>2</sub>, Zn/NaOH, Pd/H<sub>2</sub>.



The reduction of nitroalkane or nitrobenzene in neutral medium gives hydroxyl amines.

### (ii) Ammonolysis of alkyl halides



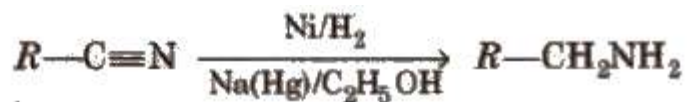
Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt.

However, primary amine is obtained as a major product by taking large excess of NH<sub>3</sub>.

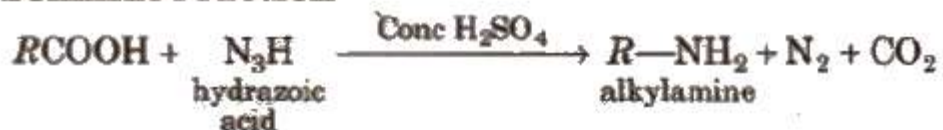
Order of reactivity of halides with amines is RI > RBr > RCl.

Aromatic amines could not be prepared since aryl halides are much less reactive towards nucleophilic substitution reactions.

### (iii) Reduction of nitriles or cyanides

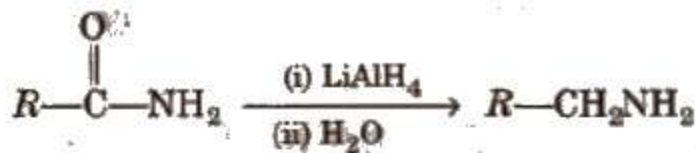


### (iv) Schmidt reaction

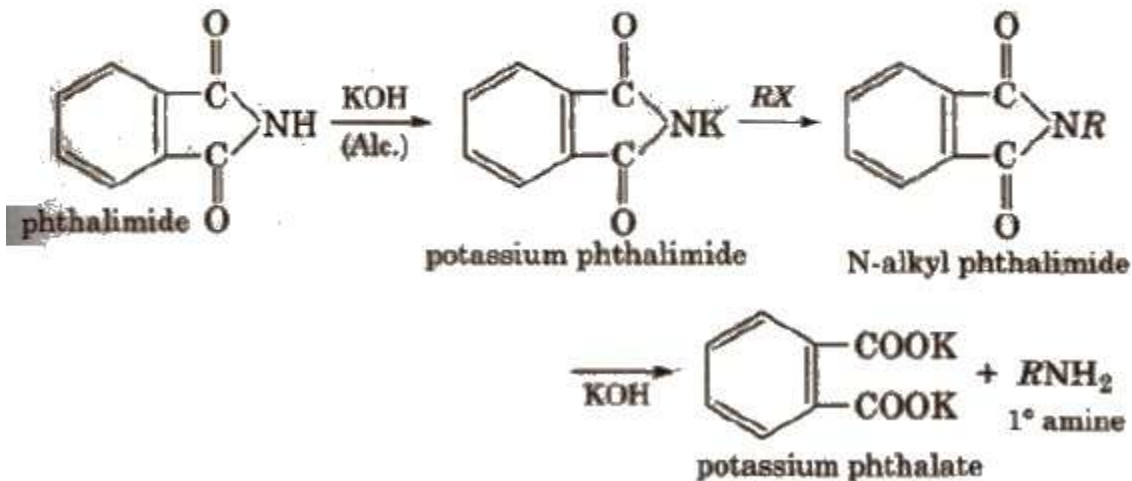


It is a modification of Curtius degradation.

### (v) Reduction of amides

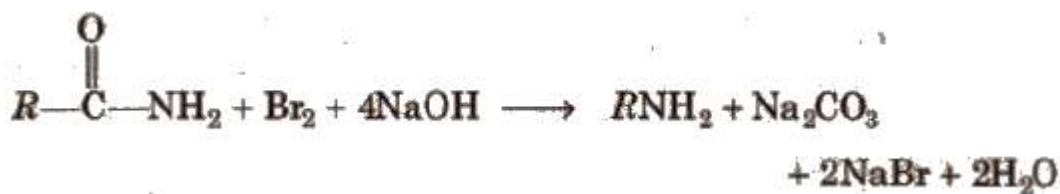


### (vi) Gabriel's phthalimide reaction



It only produces 1° amines. This method is not suitable for 1° arylamine because aryl halide does not give nucleophilic substitution reaction.

### (viii) Hofmann bromamide degradation reaction



In Hofmann degradation reaction, the amine formed has one carbon less than the parent amide. To obtain primary amine with same number of carbon atoms from primary amide, reduction is done with LiAlH<sub>4</sub>/ether.

### Physical Properties of Amines

1. The lower aliphatic amines are gases with fishy smell.
2. Primary amines with three or more carbon atoms are liquid and higher members are all solids.
3. Lower aliphatic amines are water soluble because they can form hydrogen bonds with water molecules, however the solubility decreases with increase in hydrophobic alkyl group.
4. Boiling points order primary > secondary > tertiary

5. Tertiary amines does not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation.

## Basic Strength of Amines

Amines act as Lewis bases due to the presence of lone pair of electrons on the nitrogen atom.

More the  $K_b$  (dissociation constant of base), higher is the basicity of amines.

Lesser the  $pK_b$ , higher is the basicity of amines.

Aliphatic amines ( $\text{CH}_3\text{NH}_2$ ) are stronger bases than  $\text{NH}_3$  due to the electron releasing +/- effect of the alkyl group.

Among aliphatic methyl amines, the order of basic strength in aqueous solution is as follows



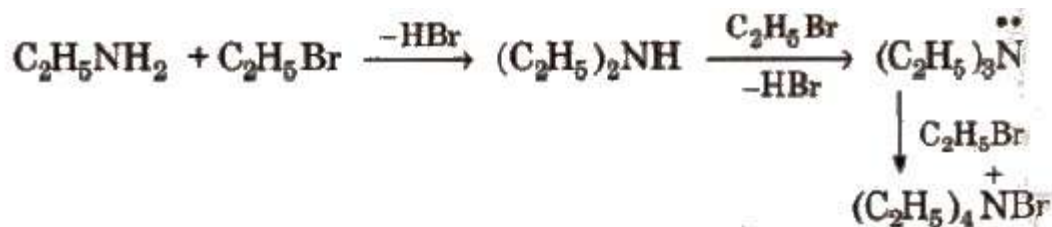
Aromatic amines are weaker bases than aliphatic amines and  $\text{NH}_3$ , due to the fact that the electron pair on the nitrogen atom is involved in resonance with the  $\pi$ -electron pairs of the ring.

Electron releasing groups (e.g.,  $-\text{CH}_3$ ,  $-\text{OCH}_3$ ,  $-\text{NH}_2$  etc.) increase the basic strength of aromatic amines while electron withdrawing groups (like  $-\text{NO}_2$ ,  $-\text{X}$ ,  $-\text{CN}$  etc.) tend to decrease the same.

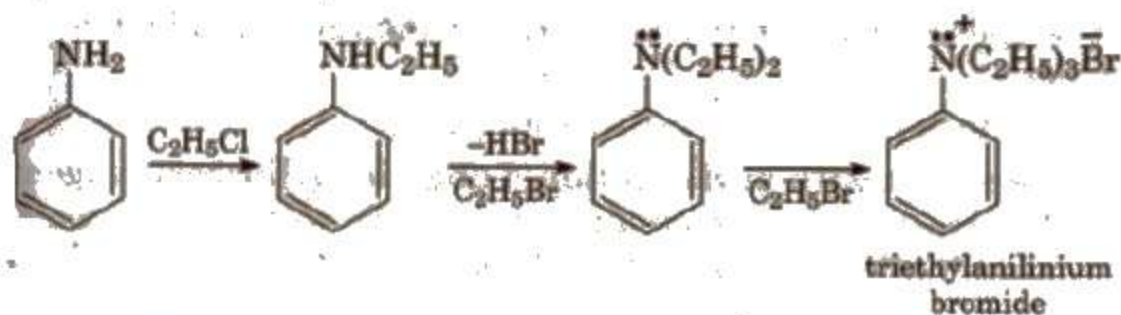
o-substituted aromatic amines are usually weaker bases than aniline irrespective of the nature of substituent whether electron releasing or electron withdrawing. This is called ortho effect and is probably due to steric and electronic factors.

## chemical Properties of Amines

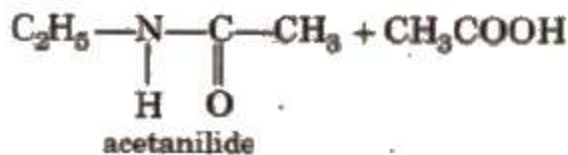
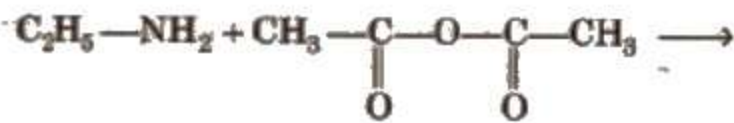
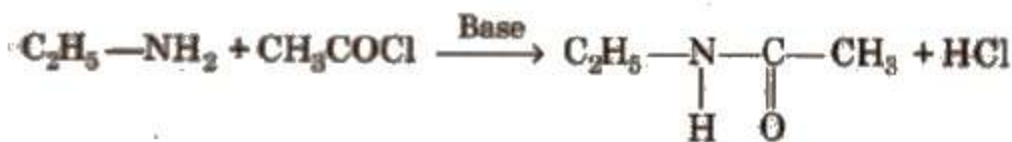
(i) **Alkylation** All the three types of amines react with alkyl halides to form quaternary ammonium salt as the final product provided alkyl halide is present in excess.



Aromatic amines also undergo alkylation as given below.



**(ii) Acylation**

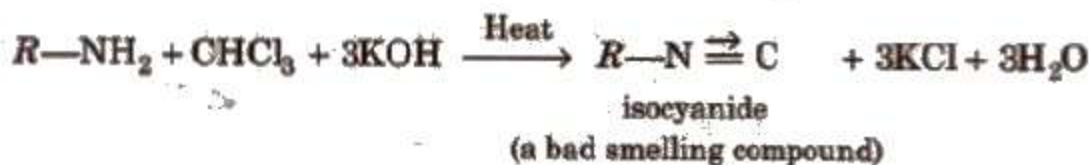


**(iii) Benzoylation**



Benzoylation of aniline is known as **Schotten Baumann reaction**.

**(iv) Carbylamine reaction [only by 1° amines]**

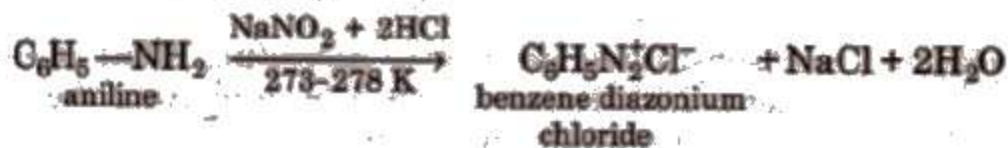


MIC or methyl isocyanate gas ( $\text{CH}_3\text{—N}=\text{C}=\text{O}$ ) was responsible for Bhopal gas tragedy in December 1984.

**(v) Reaction with nitrous acid**



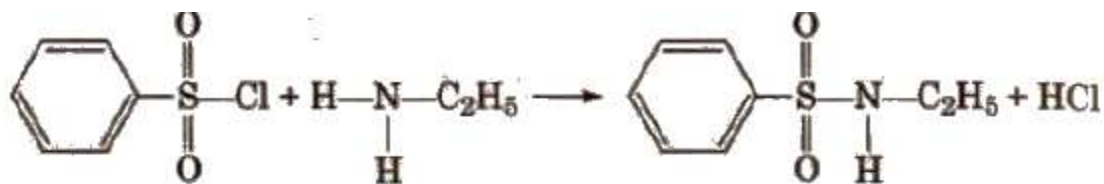
Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.



But secondary and tertiary amines react with nitrous acid in different manner.

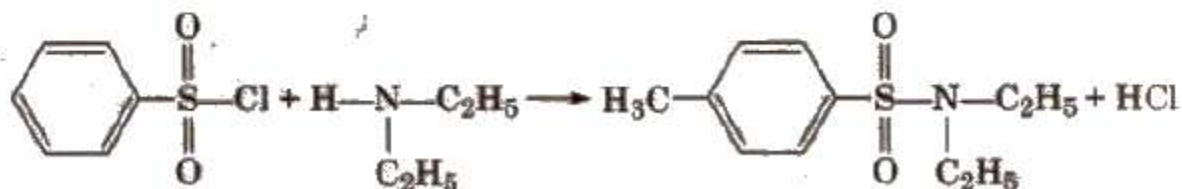
Methyl amine give dimethyl ether with  $\text{HNO}_2$ .

**(vi) Reaction with aryl sulphonyl chloride** [Hinsberg reagent] The reaction of benzenesulphonyl chloride with primary amine yield N-ethyl benzenesulphonyl amide.



(soluble in alkali)

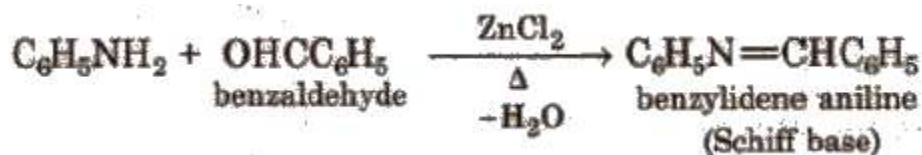
The reaction of benzenesulphonyl chloride with secondary amine yields N,N-diethyl benzene sulphonamide.



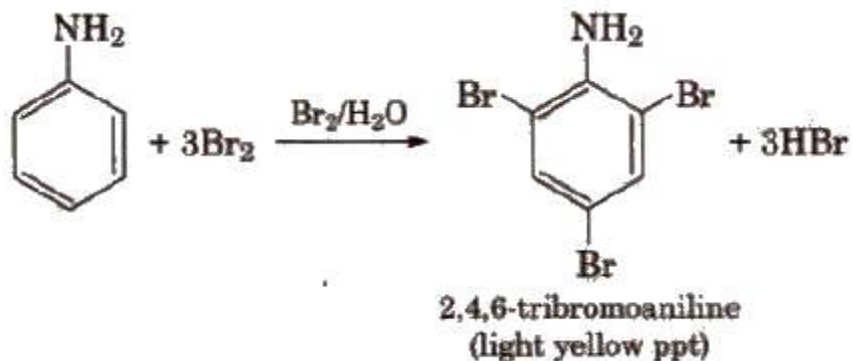
(insoluble in alkali)

Tertiary amines does not react with benzenesulphonyl chloride.

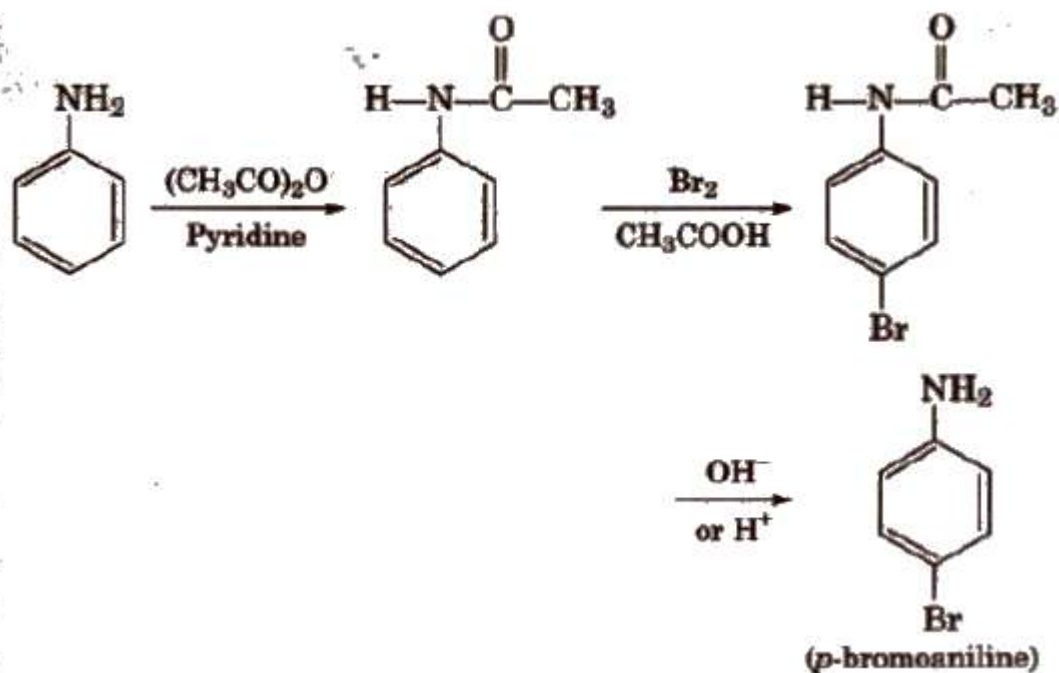
**(vii) Reaction with aldehydes** Schiff base is obtained.



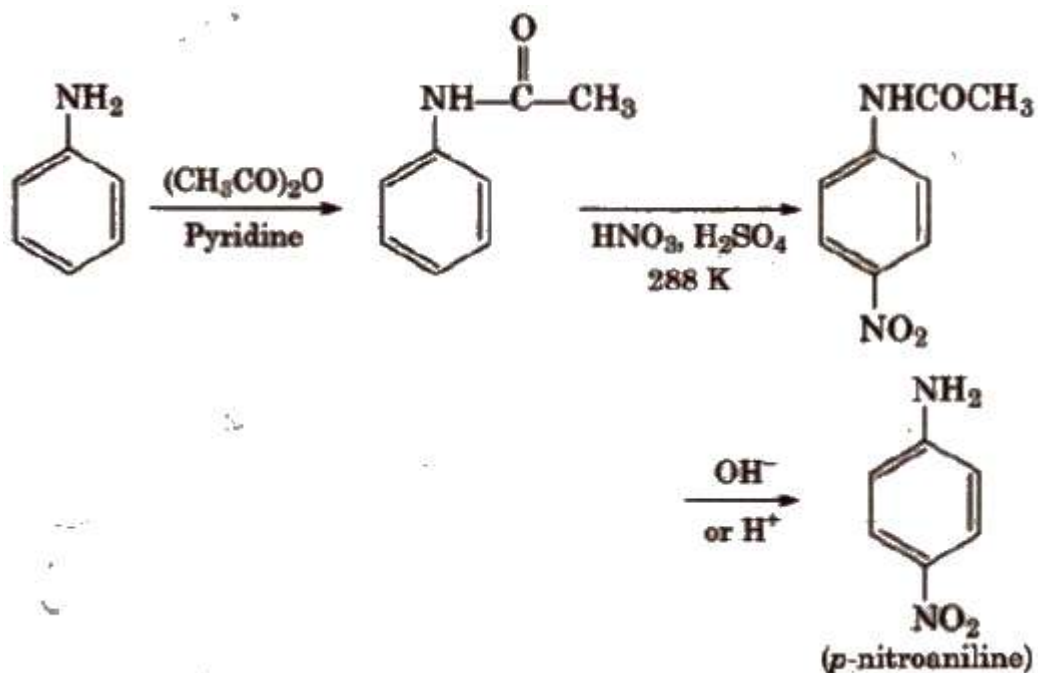
**(viii) Electrophilic substitution reactions** Aniline is ortho and para directing towards electrophilic substitution reaction due to high electron density at ortho and para-positions.



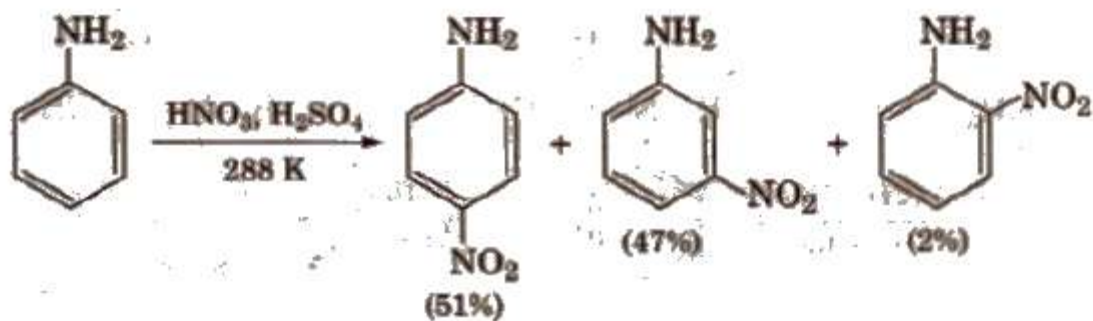
To prepare monosubstituted derivative, activating effect of  $\text{-NH}_2$  group must be controlled. It can be done by protecting the  $\text{-NH}_2$  group by acetylation with acetic anhydride.



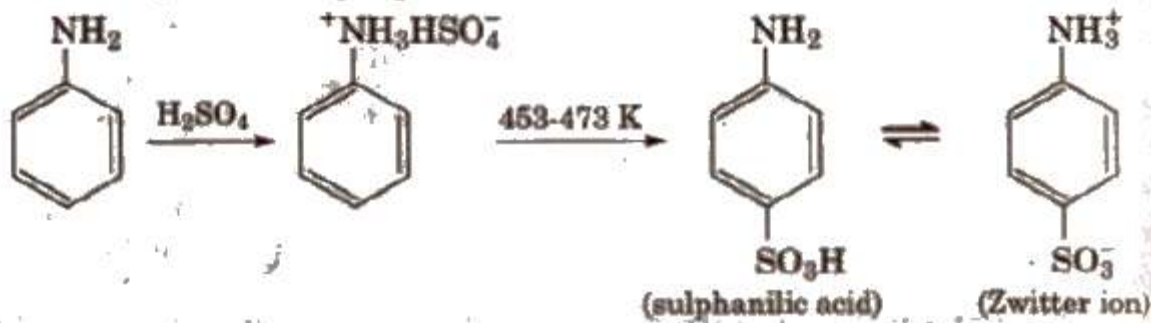
(b) **Nitration Direct** nitration of aniline is not possible as it is susceptible to oxidation, thus amino group is first protected by acetylation.



In strongly acidic medium, aniline is protonated as anilinium ion which is meta directing so it gives meta product also.



(c) **Sulphonation** On sulphonation, aniline gives sulphanilic acid, as the major product.



(d) Aniline does not undergo Friedel-Crafts reaction due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence, behave like a strong deactivating group for further chemical reaction.

(ix) **Oxidation** Use of different oxidising agents gives different products.

e.g.,

Oxidising agent	Product
Acidified $\text{KMnO}_4$ (or $\text{Na}_2\text{C}_2\text{O}_7 + \text{CuSO}_4 + \text{dil acid}$ )	Aniline black (a dye)
Chromic acid ( $\text{Na}_2\text{C}_2\text{O}_7 + \text{Conc H}_2\text{SO}_4$ )	p-benzoquinone
Caro's acid ( $\text{H}_2\text{SO}_5$ )	nitrobenzene and nitrosobenzene
Conc. nitric acid	decomposes

### Separation of Mixture of Amines ( $1^\circ$ , $2^\circ$ and $3^\circ$ )

(a) Fractional distillation This method is based on the boiling points of amines and is used satisfactorily in industry.

(b) Hofmann's method Diethyloxalate is called Hofmann's reagent with which mixture of amines is treated.

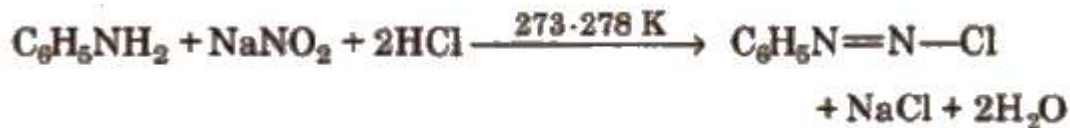


- 1° amine forms solid dialkyl oxamide (CONHR)<sub>2</sub>
- 2° amine forms liquid dialkyl oxamlc ester(CONR<sub>2</sub>-COOC<sub>2</sub>H<sub>5</sub>)
- 3° amlnes do not react

(c) Hlmsberg's method see.chemkal reactions.

### **Benzene Diazonium Chloride (C<sub>6</sub>H<sub>5</sub>N<sub>2</sub><sup>+</sup>;Cl<sup>-</sup>)**

**Preparation** (Diazotisation reaction)



The excess acid in diazotisation reaction is necessary to maintain proper acidic medium for the reaction and to prevent combination of diazonium salt formed with the undiazotised amine.

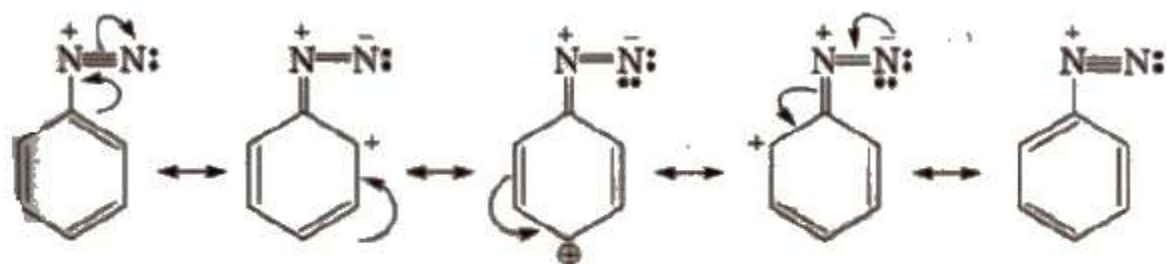
Diazonium salts are prepared and used in aqueous solutions because in solid state, they explode.

### **Properties**

It is a colourless crystalline solid, soluble in water. It has tendency to explode when dry.

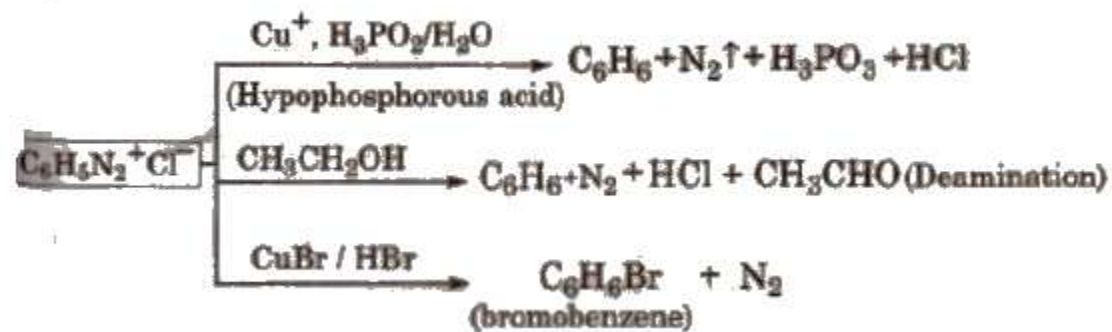
### **Stability of Arenediazonium salts**

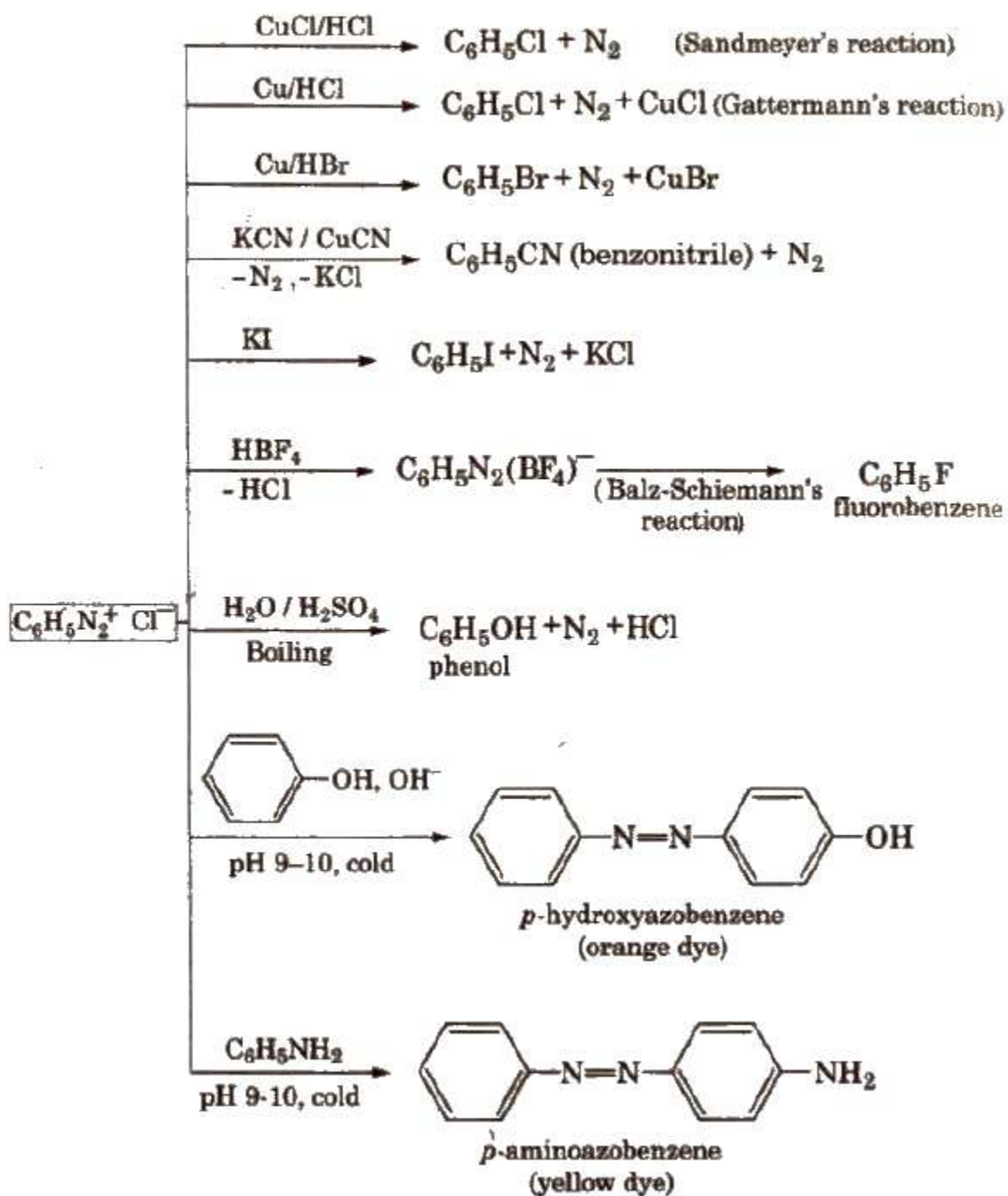
It is relatively more stable than the alkyl diazonium salt. The arenediazonium ion is resonance stabilised as is indicated by the following resonating structures:



Various resonating structures of arenediazonium ion

## Chemical Reactions

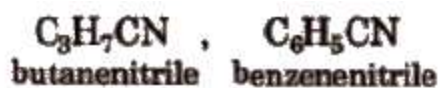




## Alkyl Cyanides'

These compound have formula RCN. These are the derivatives of RCN.

According to IUPAC system, cyanides are named as 'alkane nitrile', e.g.,

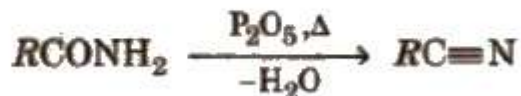


## Methods of Preparation

### (i) From alkyl halides



### (ii) From acid amides



## Physical properties

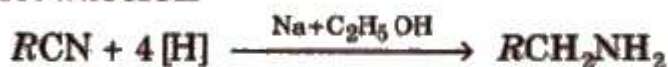
1. These are neutral compound with pleasant odour, similar to bitter almonds.
2. These are soluble in water as well as organic solvents.
3. These are poisonous but less than HCN.

## Chemical Properties

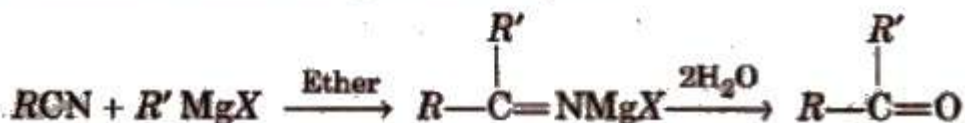
### (i) Hydrolysis



### (ii) Reduction



### (iii) Reaction with Grignard reagent



Alkyl isocyanides (RNC)

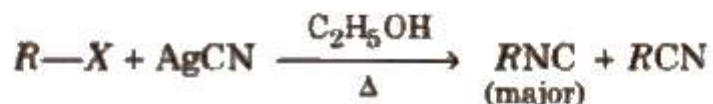
According to IUPAC system, these are named as 'alkane isonitrile'

e.g.,  $CH_3NC$  methyl isonitrile

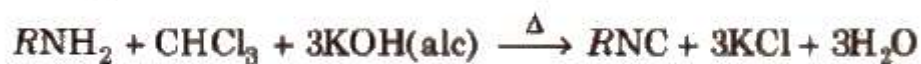
C<sub>6</sub>H<sub>5</sub>NC benzene isonitrile

## Methods of Preparation

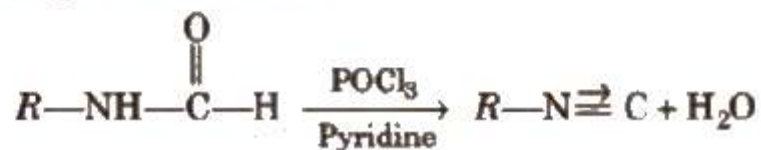
### (a) From alkyl halides



### (b) Carbylamine reaction



### (c) From N-alkyl formamide

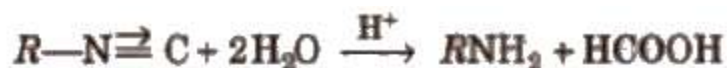


## Physical Properties

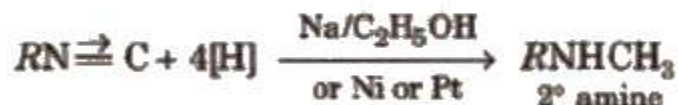
1. These are colourless unpleasent smelling liquids.
2. These are soluble in organic solvents but insoluble in water.

## Chemical Properties

### (i) Hydrolysis



### (ii) Reduction



(iii) **Addition reaction** Due to the presence of unshared pair of electrons on C atom, alkyl isocyanides give addition reaction.



(iv) **Isomerisation** At 250°C, it isomerises to nitrile.



## Nitro Compounds

These are obtained by replacing one H of hydrocarbon by  $-\text{NO}_2$  group.

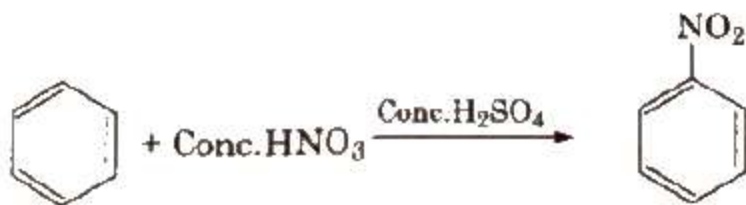
These are named according to IUPAC system as 'nitro alkane'.

### Methods of Preparation

#### (i) From alkyl halides



(ii) **Nitration** Nitrating mixture is conc  $\text{HNO}_3$  + conc  $\text{H}_2\text{SO}_4$ .



### Physical Properties

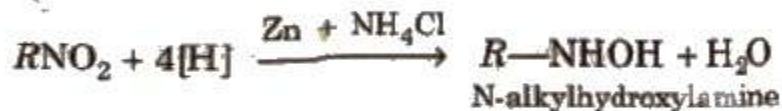
1. These are colourless pleasant smelling liquids.
2. Their boiling point are much higher than isomeric alkyl nitriles.
3. These are less soluble in water but readily soluble in organic solvents.

### Chemical Properties

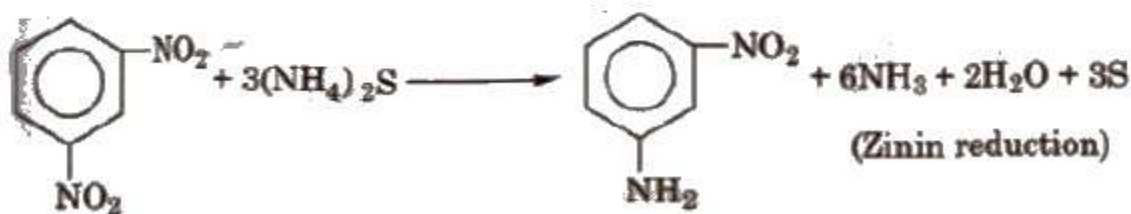
(i) **Reduction** With Sn/HCl or catalytic hydrogenation, nitroalkanes are reduced to amines.



If neutral reducing agent like Zn dust +  $NH_4Cl$  is used, hydroxylamines are obtained as major product.



In the presence of  $(NH_4)_2S$  or  $Na_2S$ , selective reduction takes place.

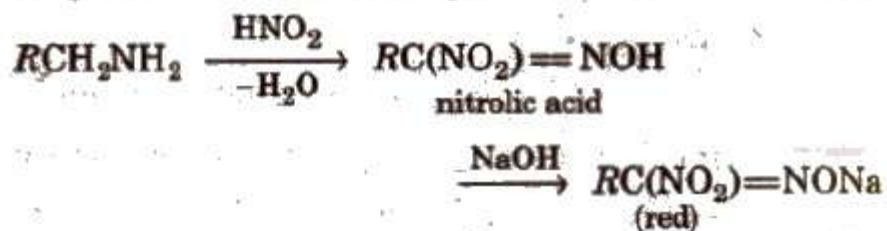


Nitrobenzene gives different products with different reagents and in different mediums.

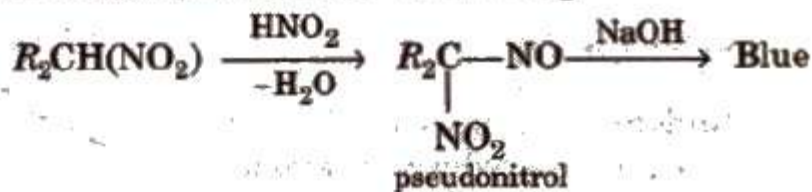
Medium	Reagent	Product
Acid	$Sn/HCl$	aniline
Neutral	$Zn/NH_4Cl$	N-phenyl hydroxylamine
Alkaline	$Na_3AsO_3/NaOH$	azoxybenzene ( $C_6H_5N=O-C_6H_5$ )
	$Zn/NaOH, CH_3OH$	azobenzene
	$Zn/NaOH, C_2H_5OH$	hydrazobenzene
Metallic hydride	$LiAlH_4$	aniline
Electrolytic	dil $H_2SO_4$	p-aminophenol

### (ii) Action of $HNO_2$

1° nitroalkane gives nitrolic acid which gives red colour with  $NaOH$ .

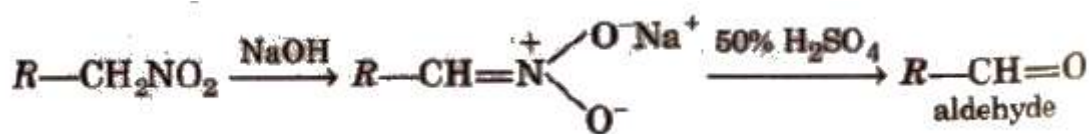


2° nitroalkanes give pseudonitrol with  $HNO_2$ .

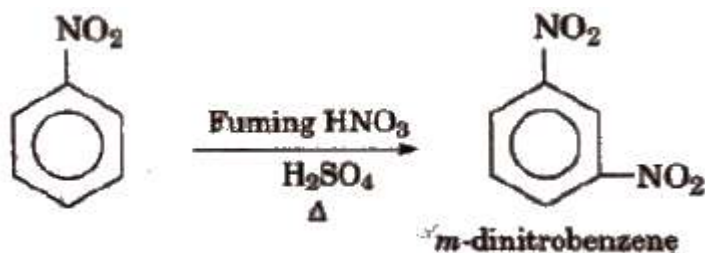


3° nitroalkanes does not react with HNO<sub>2</sub>

(iii) **Nef carbonyl** synthesis Na or K salt of 1° or 2° nitroalkanes give carbonyl compounds on acidification with 50% H<sub>2</sub>SO<sub>4</sub> at room temperature. This reaction is called Nef carbonyl synthesis.

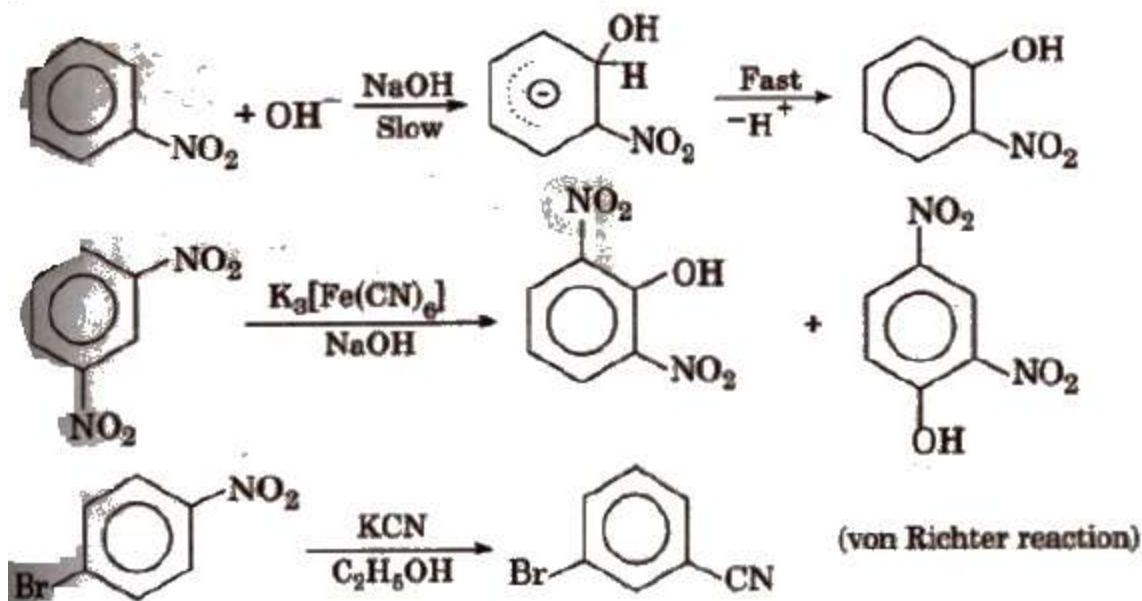


(iv) **Electrophilic** substitution On nitration, nitrobenzene gives m-dinitrobenzene (as -NO<sub>2</sub> is a m-directing group and strongly deactivating).



It does not give Friedel-Craft's alkylation.

(v) **Nucleophilic** substitution reaction -NO<sub>2</sub> group activates the ring towards nucleophilic substitution.



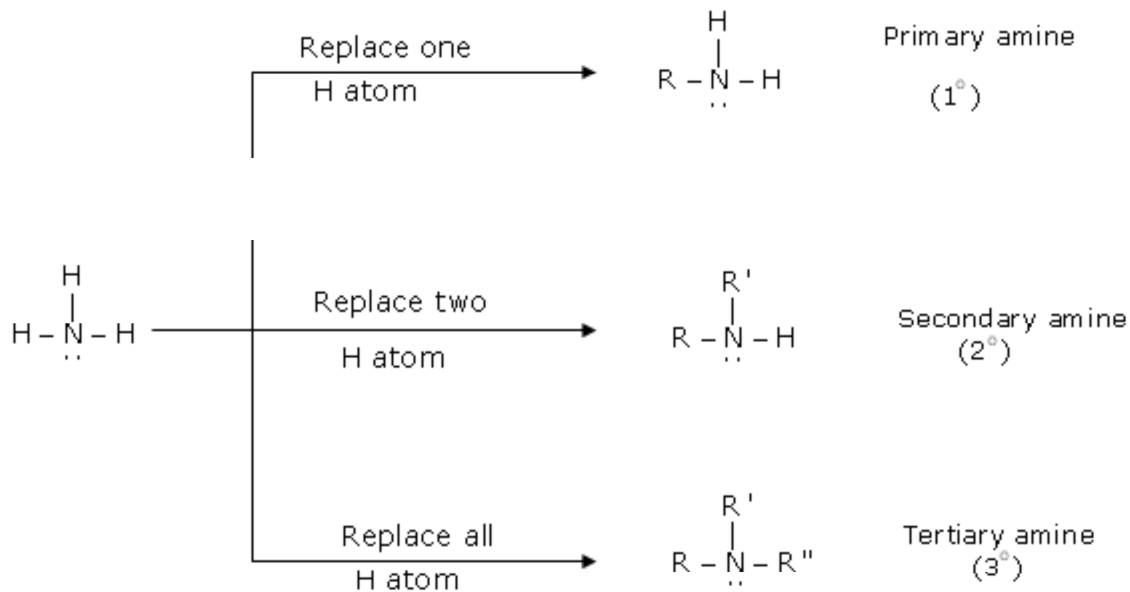


SUMMARY

- **Amines**

Amines are regarded as derivatives of ammonia in which one, two or all three hydrogen atoms are replaced by alkyl or aryl group.

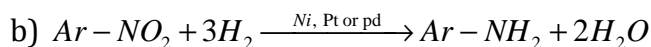
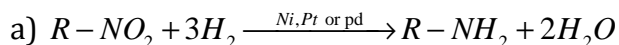
- **Classification of amines:**



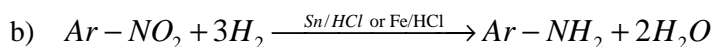
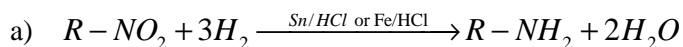
$R, R'$  and  $R''$  can be alkyl or aryl group

- **Preparation of amines:**

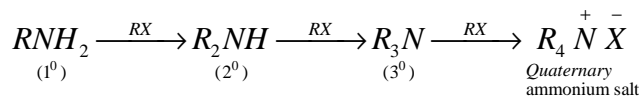
(i) By reduction of nitro compounds: Nitro compounds can be catalytically reduced by passing hydrogen gas in presence of Raney Ni, finely divided Pt or Pd as catalyst at room temperature.



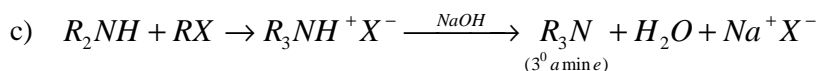
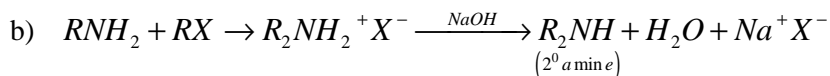
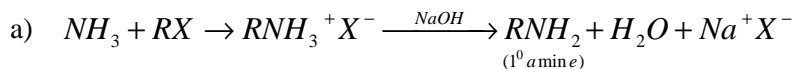
Nitro compounds can also be reduced with active metals such as Fe, Sn, Zn etc. with conc. HCl.



(ii) By Hoffmann's method (Ammonolysis of alkyl halides): Reaction of alkyl halides with an ethanolic solution of ammonia in a sealed tube at 373 K forms a mixture of primary, secondary and tertiary amine and finally quaternary ammonium salt. Process of cleavage of C-X bond by ammonia is called ammonolysis.



- The free amine can be obtained from the ammonium salt by treatment with a strong base:



- Order of reactivity of halides is: RI > RBr > RCl
- Larger the size of halogen atom easier is the cleavage of R-X bond
- Limitations of Hoffmann's method:**

Method gives mixture of amines which are difficult to separate in a laboratory.

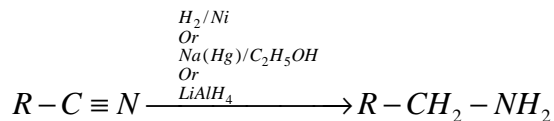
- Methods to get only one product by Hoffmann's method:**

(i) When ammonia is taken in excess primary amine is formed as main product

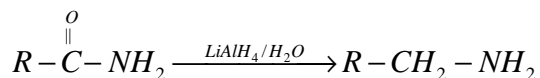
(ii) When alkyl halide is used in excess quaternary ammonium salt is formed as main product.

Method is not suitable for preparation of aryl amines because aryl amines are relatively less reactive than alkyl halides towards nucleophilic substitution reactions.

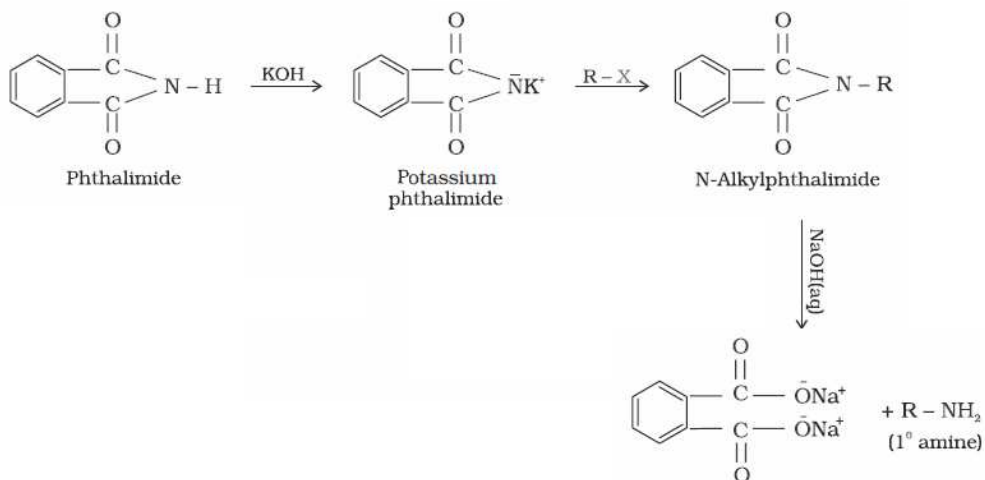
(iii) By reduction of nitriles: Nitriles can be reduced to amines using H<sub>2</sub> / Ni, LiAlH<sub>4</sub> or Na(Hg) / C<sub>2</sub>H<sub>5</sub> OH



(iii) By reduction of amides: Amides are reduced to corresponding amines by LiAlH<sub>4</sub>

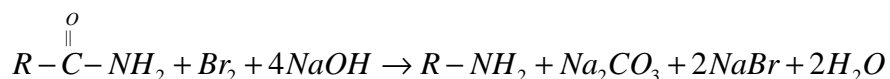


(iv) By Gabriel phthalimide synthesis: Gabriel synthesis is used for the preparation of primary amines. When phthalimide is treated with ethanolic potassium hydroxide, it forms potassium salt of phthalimide which on heating further with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.



Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with potassium phthalimide.

(v) By Hoffmann bromamide degradation reaction: Primary amines can be prepared from amides by treatment with  $\text{Br}_2$  and  $\text{KOH}$ . Amine contains one carbon atom less than the parent amide.



- **Physical properties of amines:**

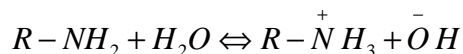
(i) Solubility: Lower aliphatic amine is soluble in water because they can form hydrogen bonding with water. Solubility decreases with increases in molar mass of amines due to increase in size of hydrophobic group

(ii) Boiling points: Among the isomeric amines primary and secondary amines have high boiling point because they can form hydrogen bonding. Tertiary amine cannot form hydrogen bonding due to the absence of hydrogen atom available for hydrogen bond formation. Hence order of boiling of isomeric amines is Primary > Secondary > Tertiary

- **Chemical properties of amines:**

(a) Basic character of amines:

Amines have an unshared pair of electrons on nitrogen atom due to which they behave as Lewis base. Basic character of amines can be better understood in terms of their  $K_b$  and  $\text{p}K_b$  values



$$K = \frac{[\text{R}-\overset{+}{\text{N}}\text{H}_3][\overset{-}{\text{O}}\text{H}]}{[\text{R}-\text{NH}_2][\text{H}_2\text{O}]}$$

$$\text{Or } K[\text{H}_2\text{O}] = \frac{[\text{R}-\overset{+}{\text{N}}\text{H}_3][\overset{-}{\text{O}}\text{H}]}{[\text{R}-\text{NH}_2]}$$

$$K_b = \frac{[\text{R}-\overset{+}{\text{N}}\text{H}_3][\overset{-}{\text{O}}\text{H}]}{[\text{R}-\text{NH}_2]}$$

$$pK_b = -\log K_b$$

Greater  $K_b$  value or smaller  $pK_b$  indicates base is strong.

(b) Comparison of basic strength of aliphatic amines and ammonia: Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups leading to high electron density on the nitrogen atom.

(c) Comparison of basic strength of primary, secondary and tertiary amines

(i) The order of basicity of amines in the gaseous phase follows the expected order on the basis of +I effect: tertiary amine > secondary amine > primary amine >  $NH_3$

(ii) In aqueous solution it is observed that tertiary amines are less basic than either primary or secondary amines. This can be explained on basis of following factors:

(a) Solvation effect: Greater is the stability of the substituted ammonium cation formed, stronger is the corresponding amine as a base. Tertiary ammonium ion is less hydrated than secondary ammonium ion which is less hydrated than primary amine. Thus tertiary amines have fewer tendencies to form ammonium ion and consequently are least basic.

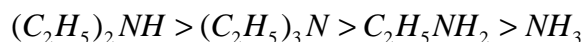
On the basis of solvation effect order of basicity of aliphatic amines should be primary amine > secondary amine > tertiary amine.

(b) Steric factor: As the crowding of alkyl group increases from primary to tertiary amine hindrance to hydrogen bonding increases which eventually decreases the basic strength. Thus there is a subtle interplay of the inductive effect, solvation effect and steric hindrance of the alkyl group which decides the basic strength of alkyl amines in the aqueous state.

When the alkyl group is small like  $CH_3$  there is no steric hindrance to hydrogen bonding. In this case order of basicity in aqueous medium is

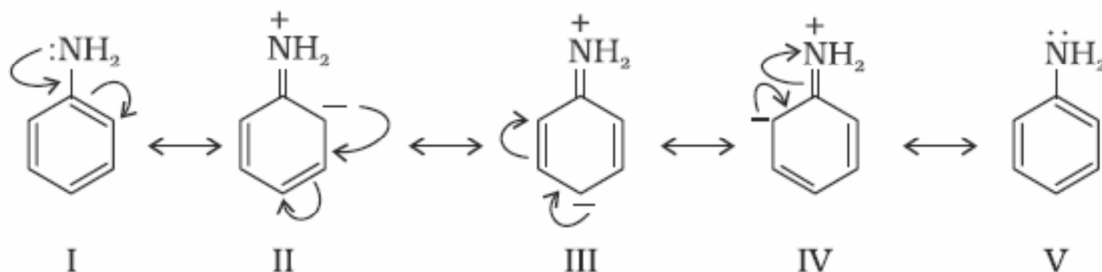


When alkyl group is ethyl group order of basicity in aqueous medium is



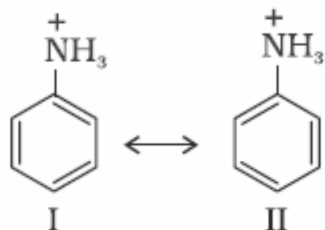
(c) Comparison of basic strength of aryl amines and alkylamines:

Generally aryl amines are considerably less basic than alkyl amines. Taking an example of aniline and ethylamine it is observed that ethyl amine is more basic than aniline. In aniline  $-NH_2$  group is directly attached to benzene ring. Hence unshared pair of electron on nitrogen is less available for protonation because of resonance. Below mentioned are resonating structures of aniline.



In the above resonating structures there is a positive charge on nitrogen atom making the lone pair less available for protonation. Hence aniline is less basic than ethyl amine which has no resonating structures. Less basicity of aniline can also be explained by comparing the relative stability of aniline and anilinium ion obtained by accepting a proton. Greater the number of resonating structures, greater is the stability of that species.

Aniline is resonance hybrid of five resonating structures whereas anilinium ion has only two resonating structures.



Thus aniline has less tendency to accept a proton to form anilinium ion.

(d) Effect of substituent on basic character of amines:

Electron donating or electron releasing group/groups (EDG) increases basic strength while electron withdrawing (EWG) decreases basic strength.

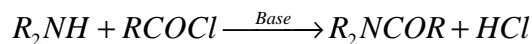
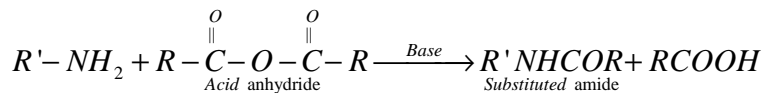
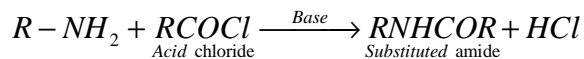


EDG =  $-\text{CH}_3, -\text{OCH}_3, -\text{NH}_2$

EWG =  $-\text{NO}_2, -\text{CN}, -\text{X} (\text{Halogen})$

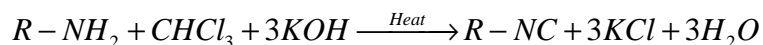
- **Reactions of amines:**

(a) Acylation Reaction: Aliphatic and aromatic primary and secondary amines (which contain replaceable hydrogen atoms) react with acid chlorides, anhydrides and esters to form substituted amide. Process of introducing an acyl group ( $\text{R}-\text{CO}-$ ) into the molecule is called acylation. The reaction is carried out in the presence of a stronger base than the amine, like pyridine, which removes  $\text{HCl}$  formed and shifts the equilibrium to the product side.



Since tertiary amine do not contain replaceable hydrogen atom they do not undergo acylation reaction.

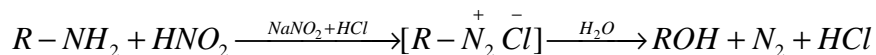
- (b) Carbylamine reaction: Only aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines.



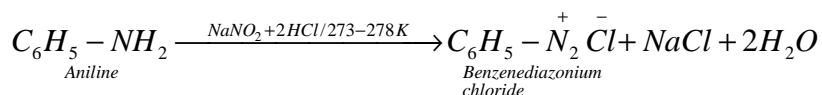
Secondary and tertiary amines do not give the above test.

- (c) Reaction of primary amine with nitrous acid:

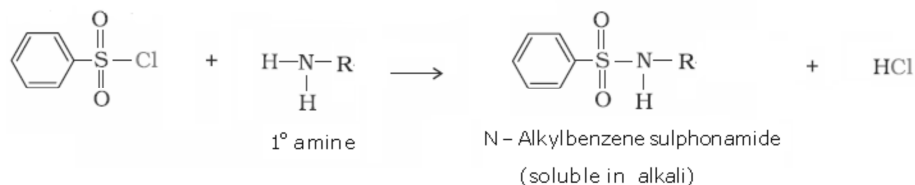
(i) Primary aliphatic amine on reaction with nitrous acid ( $HNO_2$ ) forms aliphatic diazonium salt which decomposes to form alcohol and evolve nitrogen.



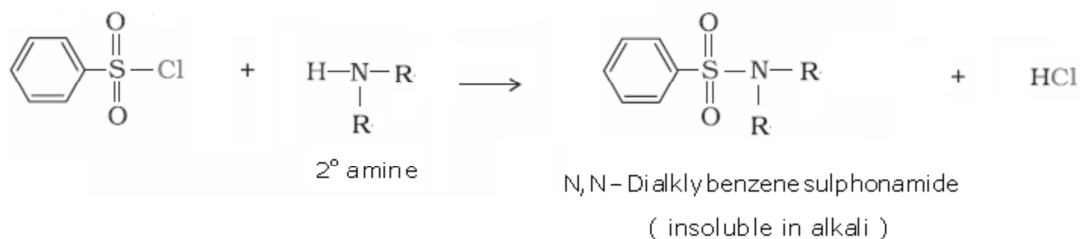
(ii) Primary aromatic amines react with nitrous acid ( $HNO_2$ ) in cold (273-278 K) to form diazonium salt.



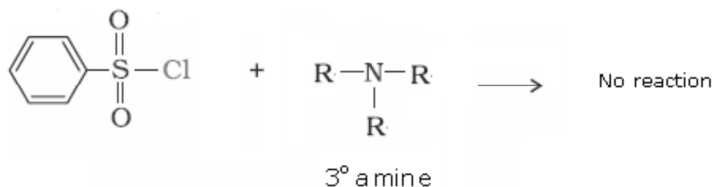
- (d) Reaction with benzene sulphonyl chloride: Hinsberg's reagent-Benzenesulphonyl chloride ( $C_6H_5SO_2Cl$ ) reacts with primary and secondary amines to form sulphonamides.



The hydrogen attached to nitrogen in sulphonamide formed by primary amine is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.



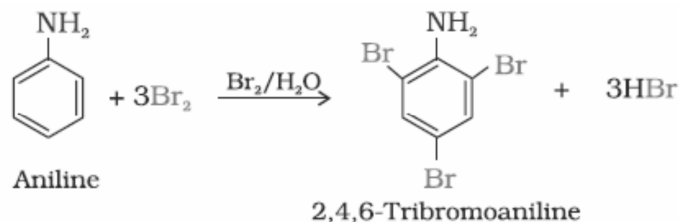
Since sulphonamide formed by secondary amine does not contain any hydrogen atom attached to nitrogen atom, so it is not acidic. Hence it is insoluble in alkali.



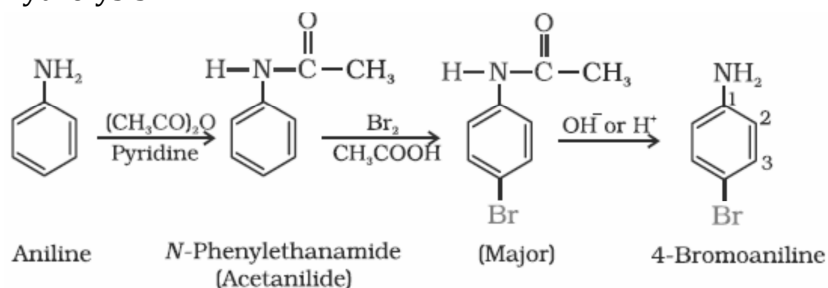
- **Ring substitution in aromatic amine:**

Aniline is more reactive than benzene and undergoes electrophilic substitution reaction preferably at ortho and para position.

(i) Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoaniline

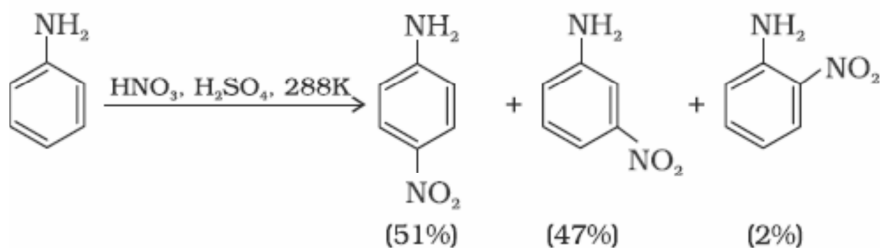


In order to stop reaction at monosubstitution activating effect of -NH<sub>2</sub> group is reduced by acetylation. This prevents di and tri substituted products. Acetyl group is removed by hydrolysis.



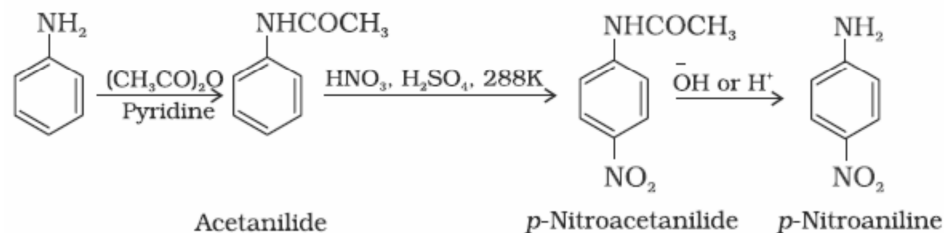
(ii) Nitration:

(a) Under strongly acidic medium aniline gets protonated to form anilinium ion, which is deactivating group and is meta directing. Hence m-nitroaniline is also formed in 47 % along with ortho and para products.



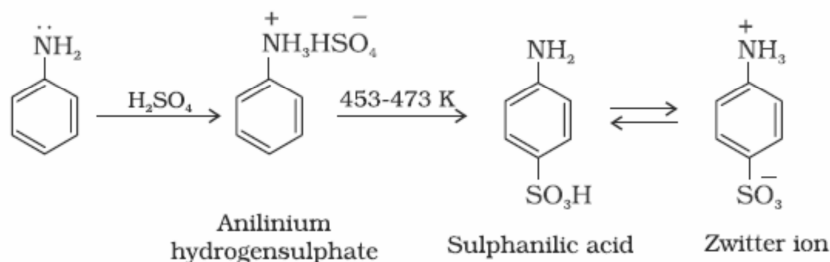
Aromatic amines cannot be nitrated directly because HNO<sub>3</sub> being a strong oxidising agent oxidises it forming black mass.

(b) Nitration by protecting the -NH<sub>2</sub> group by acetylation reaction with acetic anhydride:



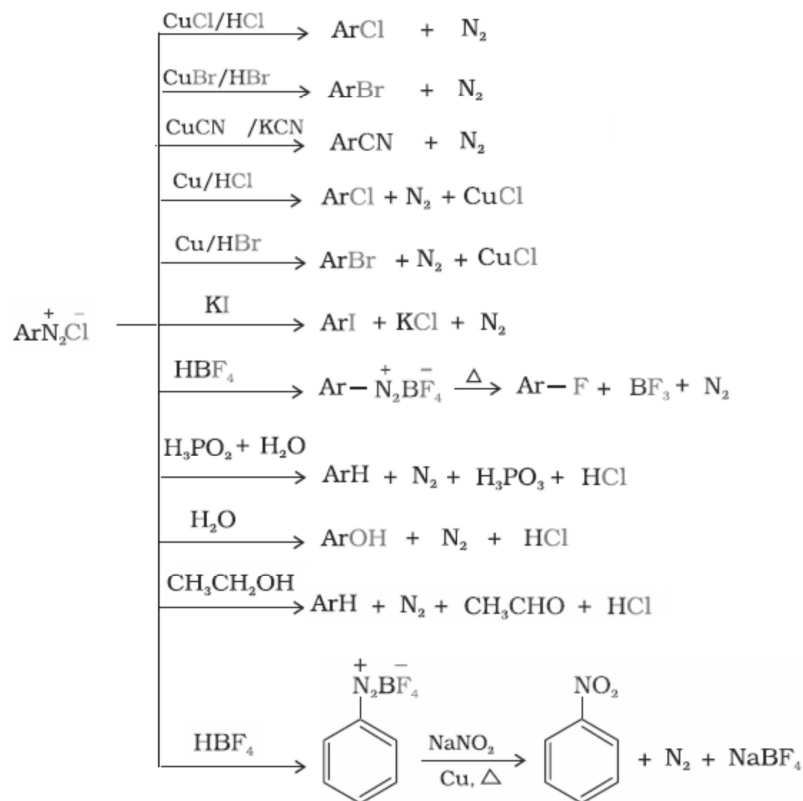
(iii) Sulphonation: Aniline reacts with conc. H<sub>2</sub>SO<sub>4</sub> to form anilinium hydrogensulphate which on heating with sulphuric acid at 453-473K produces *p*-aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product.





• **Reactions of benzene diazonium chloride:**

(a) Reactions involving displacement of nitrogen:



(b) Reactions involving retention of diazo group, coupling reactions: Diazonium ion acts as an electrophile because there is a positive charge on terminal nitrogen. Therefore benzene diazonium chloride couples with electron rich compounds like phenol and aniline to give azo compounds. Azo compounds contain  $-\text{N}=\text{N}-$  bond and reaction is coupling reaction.

